Engineering Eggshells for Carbon Dioxide Capture, Hydrogen Production, and as a Collagen Source

A Bachelors of Science Thesis

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Abstract

The burning of fossil fuels leads to greenhouse gas (GHG) emissions, like carbon dioxide (CO_2), which contribute to global warming. Current CO_2 mitigation practices comprise of: [a] separation, [b] transportation, and [c] sequestration. Presently CO_2 separation costs play a dominant role in the CO_2 management scheme. The focus of this investigation is to effectively utilize chicken eggshells, a bio-composite material rich in calcium, as a sorbent for CO_2 capture. The eggshells offer a unique combination of sorbent strength and reactivity while maintaining a low cost. The reaction mechanism consists of a series of carbonation-calcination reactions (CCR): calcium oxide (CaO) reacts with CO_2 forming calcium carbonate ($CaCO_3$), then calcining the shell forms a pure CO_2 stream and regenerates CaO. Taking advantage of the eggshell's capacity to capture CO_2, can also lead to enhanced hydrogen (H_2) production at high temperatures in a coal gasification process.

Treating the eggshell with acetic acid at low concentrations not only facilitates membrane removal, but also shows an increase in the eggshell reactivity, which leads to increased CO_2 capture as well as improved H_2 production. In addition, the membrane contains collagen which is used in skin grafting, cornea repair, osteoporosis treatment, and other medical and surgical procedures.

Overall, this study focuses on potential of treated eggshells as calcium-based sorbents for CO_2 capture and H_2 production and as source of collagen. Data shows that eggshells treated with acetic acid, not only enhances membrane removal from the shell but also leads to increased reactivity over multiple CCR cycles. The 2 molar 15 minute

treated eggshell sample shows the highest capture capacity over time. Using eggshell as a sorbent for H_2 production shows that 100% conversion of CO to H_2 can be achieved.

For my parents, Mark and Judy, without whom I would not be where I am today.

Acknowledgments

I would first like to thank Dr. Liang-Shih Fan for giving me the opportunity to participate in Undergraduate Research in his group. I have learned a great deal and have been inspired to continue my education. He has allowed me to present my work at various arenas and he served on my defense committee and I appreciate both of those things as well. I would also like to thank Dr. Hal Walker for being my advisor and friend throughout my Honduras project and also my graduate school process. I would like to express my gratitude for Dr. Walker serving on my defense committee. My appreciation also extends to all the faculty and staff that have advised and mentored me throughout my undergraduate career.

My gratitude extends to all the members of Dr. Fan's research group; they helped me learn, contributed to my project, and made my research experience a lot of fun. I could not have accomplished what I have without Mahesh Iyer. He was instrumental in my learning experience and all that I achieved. Also, thank you to Shwetha Ramkumar for being a wonderful mentor to me.

I also wish to thank all of my family and friends, both in St. Louis and Columbus. My friends and roommates have always been there for me and have been a great support. No words could express how much I appreciate all that my family has done for me. They are truly the greatest support system I could ever have. I would like to thank my extended family, even those that cannot be with me today. Lastly, I wish to express my appreciation for my fiancé for all he has done for me in the last several years. He has been there to support, advise, and encourage me.

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Chapter 1: Introduction and Motivation

1.1 CO_2 Separation and Sequestration

Fossil fuel combustion leads to greenhouse gas emissions, like carbon dioxide (CO_2), which contribute to global warming. The greenhouse gas effect is a naturally occurring effect, however, with increased GHG concentrations, an increased greenhouse effect is seen. Figure 1.1 is a representation of pollution emissions into the atmosphere. In Figure 1.2, the greenhouse effect is illustrated (Sparks, 2005).

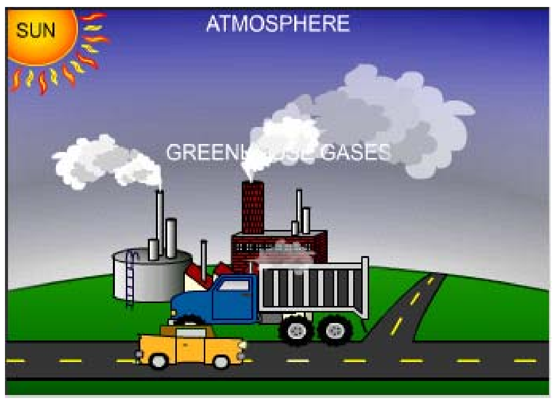

Figure 1.1 Schematic of Pollution Emissions into Atmosphere

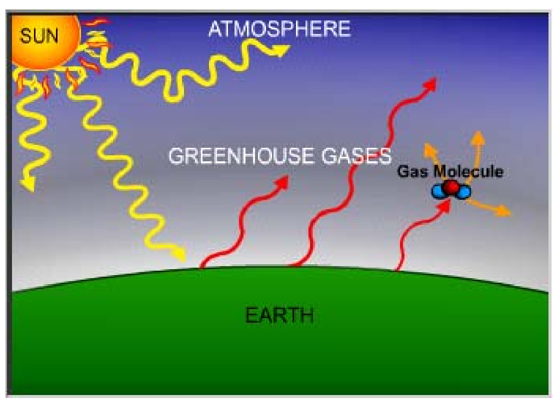

Figure 1.2 The Greenhouse Effect

In 2006, Ohio was named the number one state for air pollution, predominantly due to fossil fuel combustion (Hunt, 2006) and consistently in the top five states for emissions of CO_2. In 1995, the United States' CO_2 emissions was nearly 6 gigatons/year (Sparks, 2005), the highest country in the world. However, it has been estimated that China's emissions will soon surpass the emissions from the US. The current concentration level of CO_2 in the atmosphere is 380 ppm and is rising at 2 ppm per year. As mentioned, these increased levels of GHG's result in increased greenhouse effect (global warming), and it was projected by the IPCC in 2007 that even if the levels in 2000 would have been held constant, an increase of global temperature of 0.1°C per decade would still occur.

The current CO_2 mitigation scheme consists of: separation, transportation, and sequestration. Presently, CO_2 separation costs play a dominant role in CO_2 management. To date, research conducted in Dr. Fan's group at OSU has demonstrated the use of a high temperature calcium based process for CO_2 capture. For this, the sorbent must meet certain criteria: [a] maintain reactivity over multiple carbonation-calcination reactions (CCR) cycles, [b] withstand high temperatures and pressures, [c] be cost-effective. Chicken eggshells have shown to meet these criteria. Additionally, the shell membrane can be extremely valuable if utilized to potential.

The focus is to effectively utilize chicken eggshells, a bio-composite material rich in calcium (Sparks, 2005), as a sorbent for CO_2 separation. The eggshells offer a unique combination of sorbent strength and reactivity while maintaining a low cost. The reaction mechanism consists of a series of carbonation-calcination reactions (CCR): CaO reacts with CO_2 forming $CaCO_3$, then calcining the shell forms a pure CO_2 stream and regenerates the CaO sorbent.

Carbonation: $\mathbf{CaO + CO_2 \rightarrow CaCO_3}$ **(1)**

Calcination: $\mathbf{CaCO_3 \rightarrow CaO + CO_2}$ **(2)**

There are several alternatives to calcium-based sorbent CO_2 separation, which consist of membrane and cryogenic separation, adsorption, absorption and others. However, many of these methods can increase the net cost of energy production because they are very energy intensive. Most require high pressure and low temperature to increase CO_2 solubility. Yet, with a reaction-based system, the separation occurs at high temperature and low pressures, eliminating the cost intensive cooling and compression (Gupta and Fan, 2002; Sparks, 2005).

After transportation, the next stage of CO_2 management is sequestration. Carbon dioxide capture and storage consist of CO_2 capture and compression from major sources. There are different types of carbon sequestration: Geological sequestration is storing CO_2 beneath the earth's surface in deep reservoirs, and it "remains the priority storage option due to low environmental risks, long storage retention times, large storage potential and maturity of the technology compared to the other storage options." Mineral sequestration is another technique that involves the chemical reaction of CO_2 with metal oxides that bind the carbon permanently. Another method is the injection into the ocean or also, simply reusing the CO_2 in industrial processes

(http://www.greenhouse.gov.au/ccs/publications/key-findings.html).

Figure 1.3 represents possible CO_2 sequestration techniques.

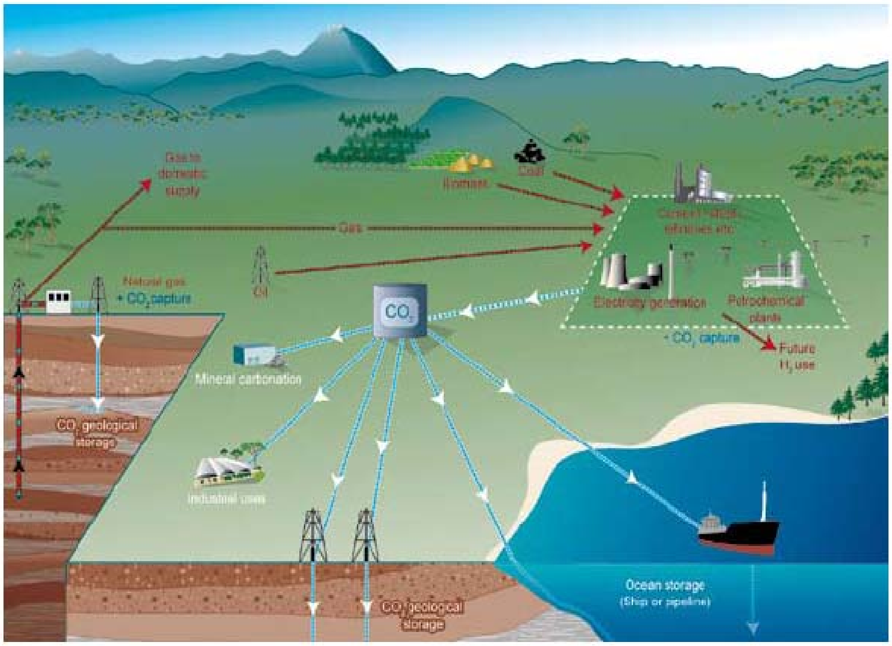

Figure 1.3. Possible CO_2 Sequestration Techniques after Capture

1.2 H_2 Production

Both the pollution concerns associated with coal and natural gas combustion and the rising energy needs facing the world and together have shifted our focus towards a hydrogen (H_2) economy. In-situ CO_2 capture, using calcium sorbents, during a coal gasification process can enhance H_2 production. Products of gasification are CO and H_2, known as “syn gas”. The water gas shift reaction (WGSR), the reaction of carbon monoxide with steam to produce H_2 and CO_2, is limited by its thermodynamic equilibrium.

$$\textbf{WGSR: } CO + H_2O \rightarrow H_2 + CO_2 \qquad \textbf{(3)}$$

It is possible to drive the WGSR forward, as can be explained by l*a-Chatelier’s* principle, by continually removing the CO_2 product using the eggshell as a sorbent. Consequently, this improves the yield of H_2 and achieves almost complete conversion of carbon monoxide. This process can effectively and economically produce a pure H_2 stream from coal gasification with integrated capture of CO_2 emissions. Figure 1.4 (Iyer,

2006) represents that. Other ways to drive the reaction forward are to have an excess reactant and also to increase the pressure.

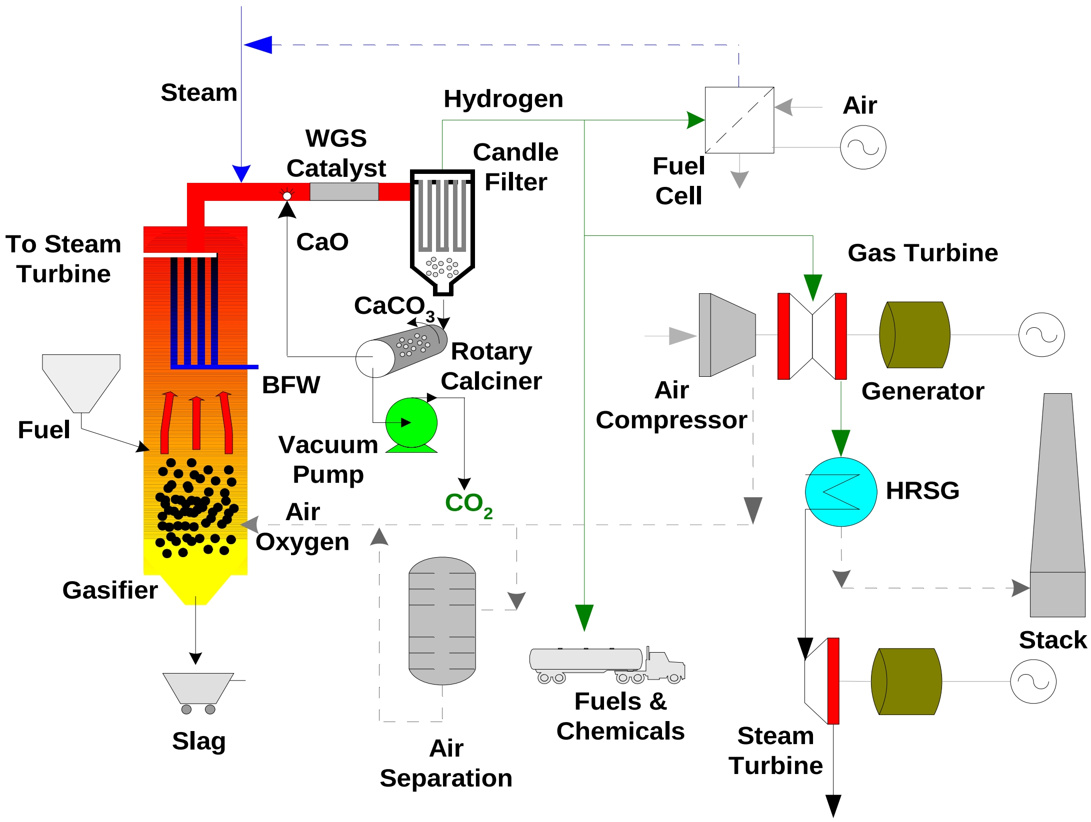

Figure 1.4. Overall Process Integration for H_2 Production

There are several potential uses of H_2. These consist of fuel cells, electrochemical conversion into electricity, as well as for combustion. When redesigned, gas turbines can utilize H_2 for power generation as well (IPCC, 2007). H_2 will become especially important in the transportation sector in the future due to the difficulty of employing of carbon capture on smaller, mobile emissions sources, as compared to a large stationary sources such as a power plant.

Unfortunately, the transportation of H_2 is still a major obstacle. There are other challenges facing the hydrogen economy now as well. There is a lack of "costcompetitive fuel cells and other hydrogen equipment" (IPCC). The US would need more than 150 million tons H_2/year, but yet only has a current production capacity of 8 million tons/year (Iyer, 2006). Safety is also a major challenge when dealing with hydrogen, due to "its high flammability..., low ignition energy, and high flame speed" (IPCC).

1.3 Effects of Climate Change

The IPCC recently released a statement saying, "Warming of the climate system is unequivocal, as is now evident from observations of increases in global average air and ocean temperatures, widespread melting of snow and ice, and rising global mean sea level."

Figure 1.5 (IPCC presentation, 2007) shows three graphs: one representing the rise of global temperature, one representing the rise of global sea level, and one representing the decline of snow cover in the Northern Hemisphere.

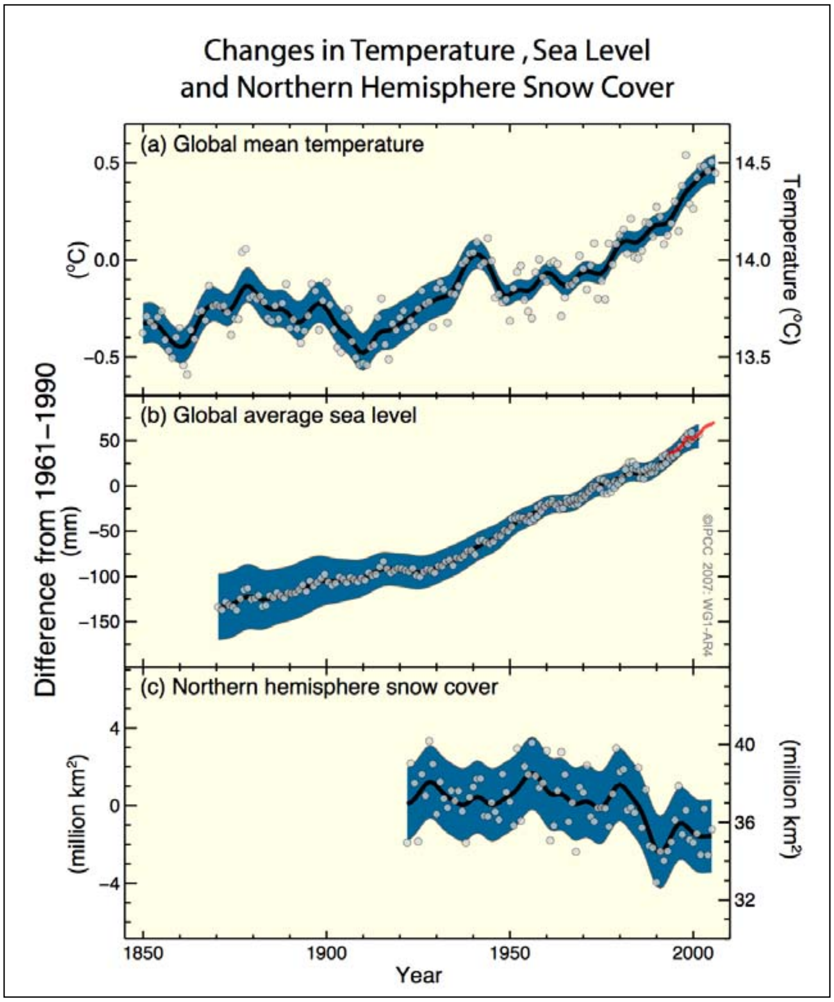

Figure 1.5. Changes in Temperature, Sea Level, and Northern Hemisphere Snow Cover

Other than the problems represented in Figure 1.5, there are many adverse effects that the world will be facing in the future, and in some cases is already seeing. Some of these effects are:

- “Significantly increased precipitation in eastern parts of North and South America, northern Europe and northern and central Asia,
- Drying in the Sahel, Mediterranean, southern Africa and parts of southern Asia, and
- More intense and longer droughts observed since the 1970s, particularly in the tropics and subtropics” (IPCC, 2007).

1.4 Disposal of Eggshells

Other than personal consumption, eggs are used in many commercial arenas as well: baked goods, fast food, salad dressing and many others. Thus, the US generates roughly 190,000 tons of eggshell waste per year, thus leading to a waste disposal issue. Due to the organic properties of the eggshell and membrane, the shell is considered an organic waste leading to costly disposal, around $20-40/ton (Iyer, 2006; Miller, 2001). Another use of the eggshell is to be recycled in animal's diets as a source of calcium (Gittins, 2002) or they may also be land applied.

Implementation of this research will alleviate the problems of eggshell waste disposal by creating applications for both the waste eggshells and the organic membranes.

1.5 Project Objectives

This project had certain objectives that are outlined as follows:

1. Engineer the chicken eggshells by optimizing the acid concentration and the residence time for maximal reactivity as well as the membrane removal.
2. Analyze the membrane, separated from the eggshell, for its collagen composition and properties.
3. Study the CO_2 capture capacity of these modified eggshells under simulated flue gas conditions for multiple CCR cycles.
4. Investigate the feasibility of modified eggshell as sorbents for enhanced H_2 production.

The overall objective was to obtain a structurally modified eggshell sorbent by treating it with an organic acid while removing the collagen-containing membrane as well. The parameters varied were residence time of the eggshell sample in the acid and the acid concentration while investigating their effects on the sorbent reactivity at high temperatures towards CO_2 capture and H_2 production. In addition, their concurrent effects on the membrane properties for collagen extraction were examined.

Chapter 2: Background

2.1 Chicken Eggshells

Chicken eggshells are approximately 5.5 grams, with nearly 95% consisting of calcium carbonate. The rest of the shell consists of small amounts of phosphorous, magnesium, sodium, potassium, zinc, manganese, iron and copper. The organic matrix contributes to the structure and strength of the shell (Butcher and Miles). A picture of the eggshell can be seen in Figure 2.1 (Sparks, 2005). The eggshell is comprised of three layers: vertical (external), palisade, and mammillary (innermost) layers with thickness of ~5-8m, ~200m, and ~110m respectively (Sparks, 2005).

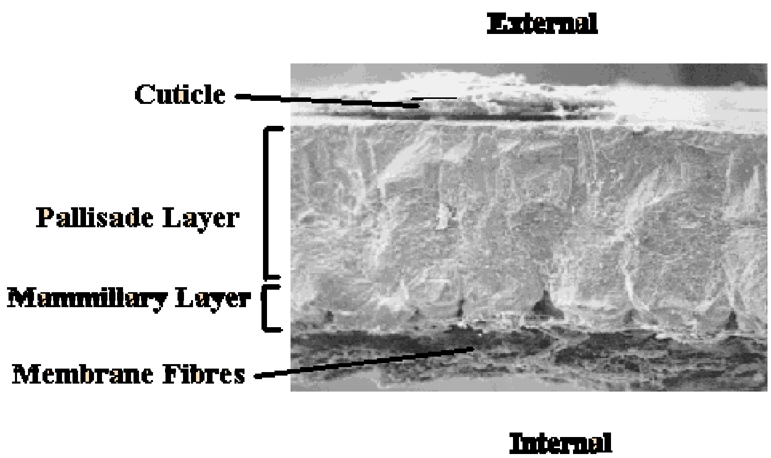

Figure 2.1 Transverse Sections of Chicken Eggshell

When the eggshell, which is predominantly calcium carbonate, is in the acetic acid solution the reaction that takes place is calcium carbonate reacting with the carboxylic acid to form calcium acetate, carbon dioxide, and water. It can be seen as follows:

$$\mathbf{CaCO_3 + 2CH_3COOH \rightarrow Ca(CH_3COO)_2 + CO_2 + H_2O} \qquad \textbf{(4)}$$

The production of the carbon dioxide bubbles is thought to enhance membrane removal as well as lead to the change of the eggshell membrane, specifically by increasing the porosity, which leads to increased reactivity over time. More will be discussed in Results and Discussion.

2.2 Collagen

Collagen is a long fiber that connects and strengthens tissues and is the most abundant protein in animals, found in bones, ligaments, skin, and cartilage. As of now, 19 different types of collagen have been found. Table 2.1 describes a few of the different types of collagen and where they are found (Kimball Pages; King, M.).

Table 2.1 Types and Location of Different Types of Collagen

Type	Location
I	Tendons, bone, skin, ligaments
II	Cartilage
III	Skin, muscle, walls of arteries and intestine
IV	Basal lamina of epithelia
V	Mostly interstitial tissue
X	Cartilage

Current uses for eggshell membrane consist of removal of reactive dyes from colored waste or eliminating heavy metal ions from solutions when waste is dilute. However, the membrane has shown to contain about 10% collagen: Type I, III, IV, V, and X, where most is type 1 and the ratio I:V = 100:1. Collagen is used in many cosmetic and surgical procedures and can cost $1000/gram (Gittins). Initial work with the Mass Spectrometry Lab at OSU has confirmed that there is collagen in the eggshell membrane, treated and untreated.

Table 2.2 summarizes the information from Triggs (2004) regarding the different sources of collagen along with their advantages and disadvantages

Table 2.2 Sources of Collagen and Their Advantages and Disadvantages

Shark Cartilage	Chickens	Bovine	Plants
Expensive	Economical	Difficult extraction	Very different from animal
Suited for cancer prevention	Suited for joint relief	Most like human	Very low adsorption
Low bio-absorbency rate		Most bio-available (~15%)	

As mentioned, there are many uses for collagen; both in cosmetic and medical procedures. In cosmetic procedures, collagen is used as a dermal filler to reduce wrinkles and scars and to augment soft tissue contours. Figures 2.2 (Inmagine) and 2.3 (Cosmedicare) show both the way of injection of collagen in a cosmetic procudeure as well as some before-and-after images.

Figure 2.2 The Utilization of Collagen for a Cosmetic Procedure as a Dermal Filler

Figure 2.3 The Before-and-After of a Cosmetic Procedure to Reduce Lines and Wrinkles in the Face

Such medical procedures that utilize collagen are angioplasty, skin grafting, cornea repair, osteoporosis treatment and many more. Figure 2.4 shows a picture of a burn victim in need of a skin graft, and Figure 2.5 represents how collagen aids in attaching the new skin over the injury. Figure 2.6 shows the same burn victim now healed. (All figures obtained from Demling et. al).

Figure 2.4 Burn Victim Requiring Skin Graft

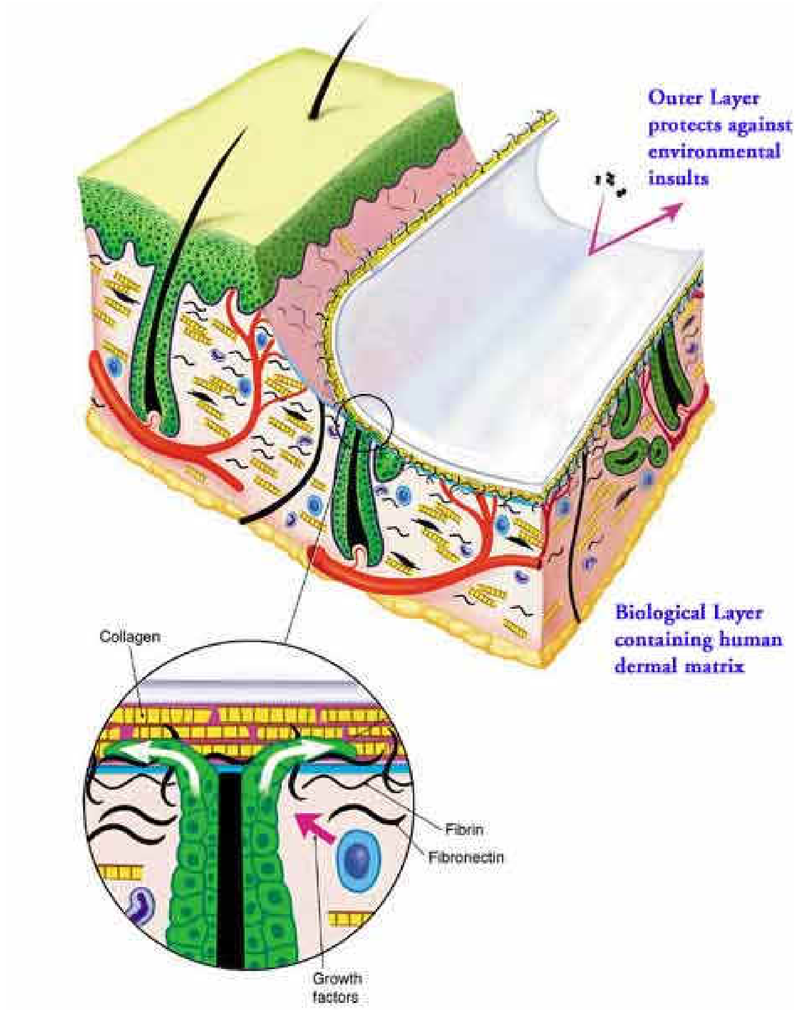

Figure 2.5 Attachment of a Skin Graft Utilizing Collagen

Figure 2.6 Healed Burn Victim After Skin Graft

2.3 Necessity of an Agglomerated Sorbent

'Flue gas, containing particulate emissions known as fly ash, is the result of coal combustion. When the micron sized calcium sorbent fines are injected into the flue gas streams to capture CO_2, they physically mix with the fly ash particles. These calcium-based sorbents are of the similar size range (0-50 microns) as compared to the fly ash particles originating from coal combustion. (Gupta et al., 2004). This is detrimental to the regenerative use of the calcium particles over several CCR cycles as they cannot be easily separated from the fly ash mixture. However, if the calcium sorbents used are of a larger particle size (1-2 mm) than the fly ash fines, their separation is possible using particle capture devices such as cyclones. This leads to the need for inexpensive agglomerated calcium-based sorbents which maintain high reactivity with CO_2' (Iyer, et al, 2005). Figure 2.7 (Iyer, 2006) demonstrates the benefit of having an agglomerated sorbent; it becomes much easier to separate than a powdered sorbent from the fly ash.

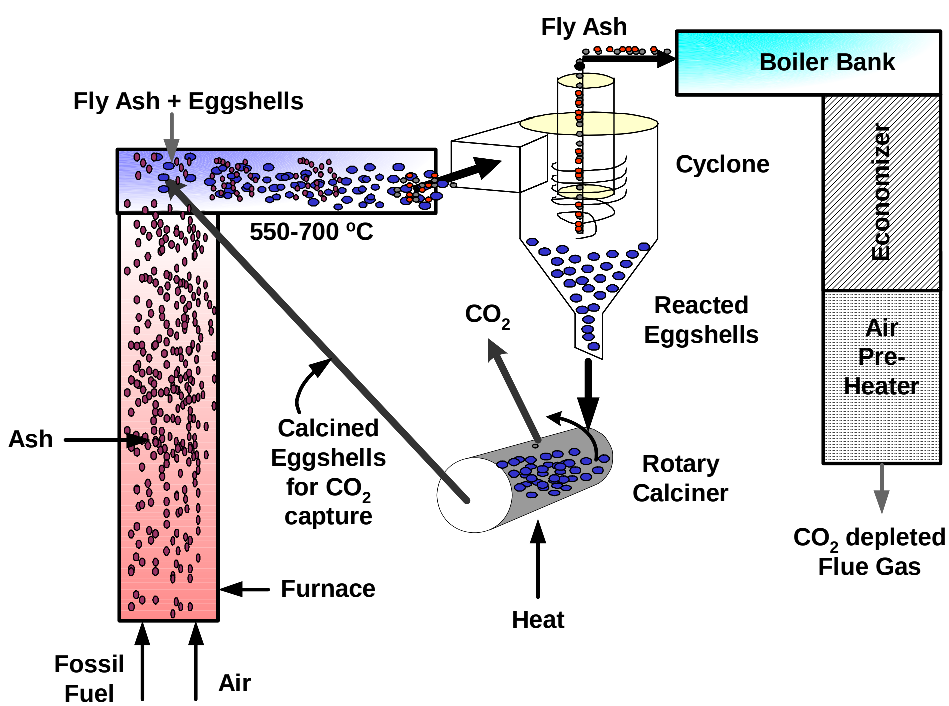

Figure 2.7 Diagram Representing Necessity for Agglomerated Sorbents for CO_2 Capture in Coal Combustion

Chapter 3: Experimental Set-up and Procedure

3.1 Experimental Procedure

a) ***Literature Review:*** This was an ongoing task and occurred over the last several quarters. The three fold focus has been on the eggshell and its membrane composition, membrane removal techniques, and applications of calcium materials toward CO_2 capture and H_2 production.

b) ***Acetic Acid Solution Preparation:*** The acetic acid solution was prepared using a 17 normal (glacial acetic acid) solution, and then mixed with appropriate amounts of distilled water to obtain the desired the concentration.

c) ***Sample Preparation and Characterization***: Chicken eggshell samples were procured from Daybreak Foods, Inc, WI, along with those obtained from household waste. The eggshells were then pre-treated in an acetic acid solution, concentrations ranging from 1 – 10 molar, by mixing in a small glass beaker on a magnetic stir plate for residence times ranging from 5-60 minutes. After desired residence time, the liquid, containing the membranes would be poured out and filtered and both the shells and the membrane would be rinsed repeatedly with distilled water. Figure 3.1 (Iyer, 2006) shows the eggshell and detached membrane in an acetic acid solution. This is how the structurally modified eggshell sorbent was synthesized while allowing for removal of the collagen-containing membrane from it. Eggshells that were untreated were simply rinsed with distilled water. Analysis of collagen content of the membrane was performed by The Mass Spectrometry Facility in Fontana Labs at OSU. Morphological and structural properties were evaluated using Scanning Electron Microscopy (SEM).

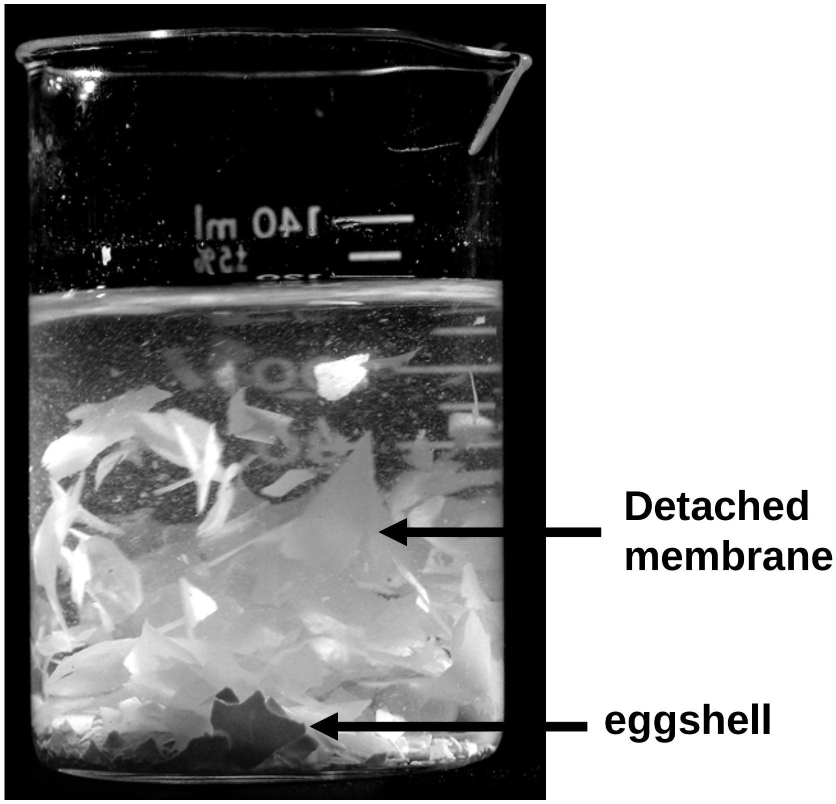

Figure 3.1 Pre-Treatment Process: Eggshell and Detached Membrane in Acetic Acid Solution

d) ***Sorbent Reactivity Testing:*** Analysis of the sorbent's reactivity for both ***1)*** CO_2 capture and ***2)*** H_2 production was conducted. Using a thermal gravimetric analyzer (TGA), shown in Figure 3.2 (Iyer), the operating conditions of flue gas can be simulated, and the reactivity of the eggshell towards carbonation was evaluated over multiple CCR cycles. By controlling the valve (switched to 1 or 2) using a timer, allows for control of the composition of gas that the sorbent is subjected to. The temperature was set to 700^{o}C and the cycle time was set to 60 minutes. A small, single piece of eggshell, usually 15-25 mg, has to be carefully placed into a basket-like container that is within the reactor tube (shown exaggerated in the figure). This instrument was connected to a computer where all of the data was sent and easily retrieved.

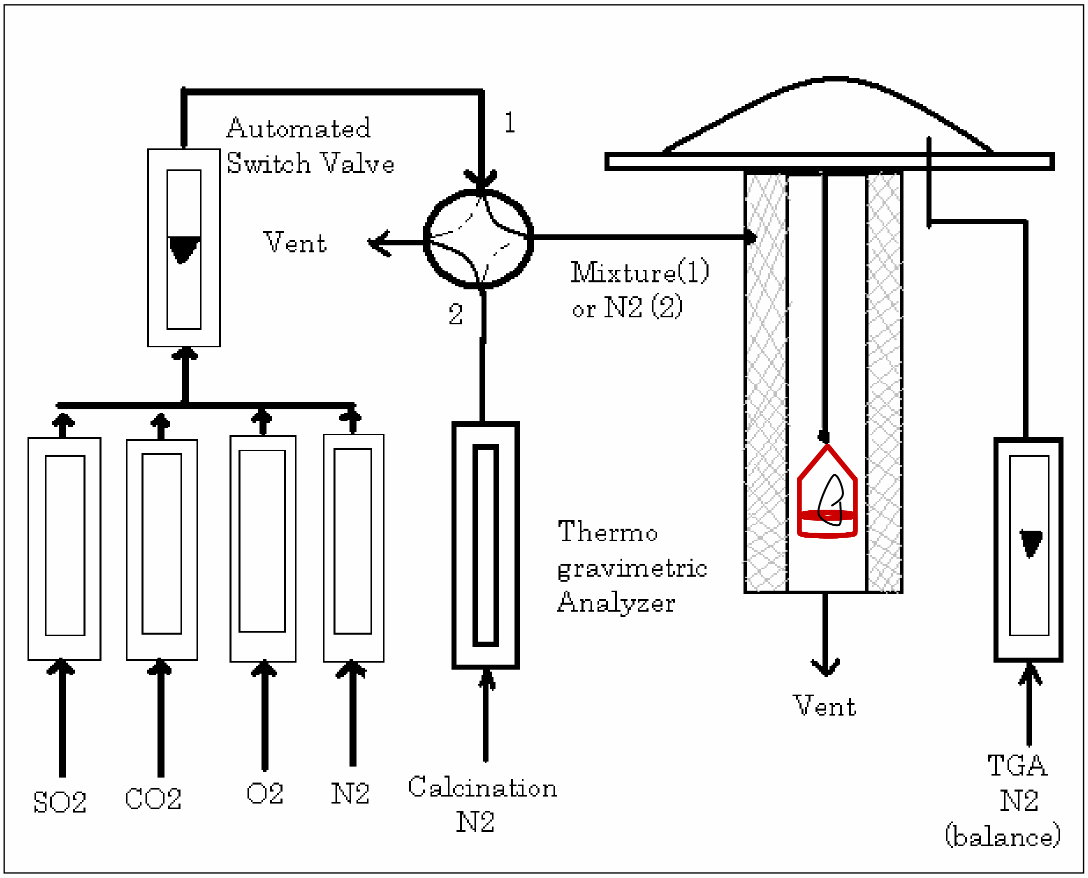

Figure 3.2. Schematic of Perkin Elmer Thermal Gravimetric Analyzer

The enhanced H_2 production testing was conducted in a fixed bed reactor, seen in Figure 3.3 (Iyer, 2006), operating at elevated temperatures and pressures. Approximately 5 grams of the desired eggshell was weighed on a balance and added to reactor tube between layers of glass wool. The eggshell was then calcined at 700°C for approximately 4 hours, before the reaction phase. The reaction was controlled by selecting the composition of the gases flowing through the fixed-bed reactor. The steam to carbon monoxide ratio was varied from 1:1 to 3:1 by setting different values on the flow controllers, and the reaction took place at 650^{o}C and 0 psig. The products were then determined using gas analyzers.

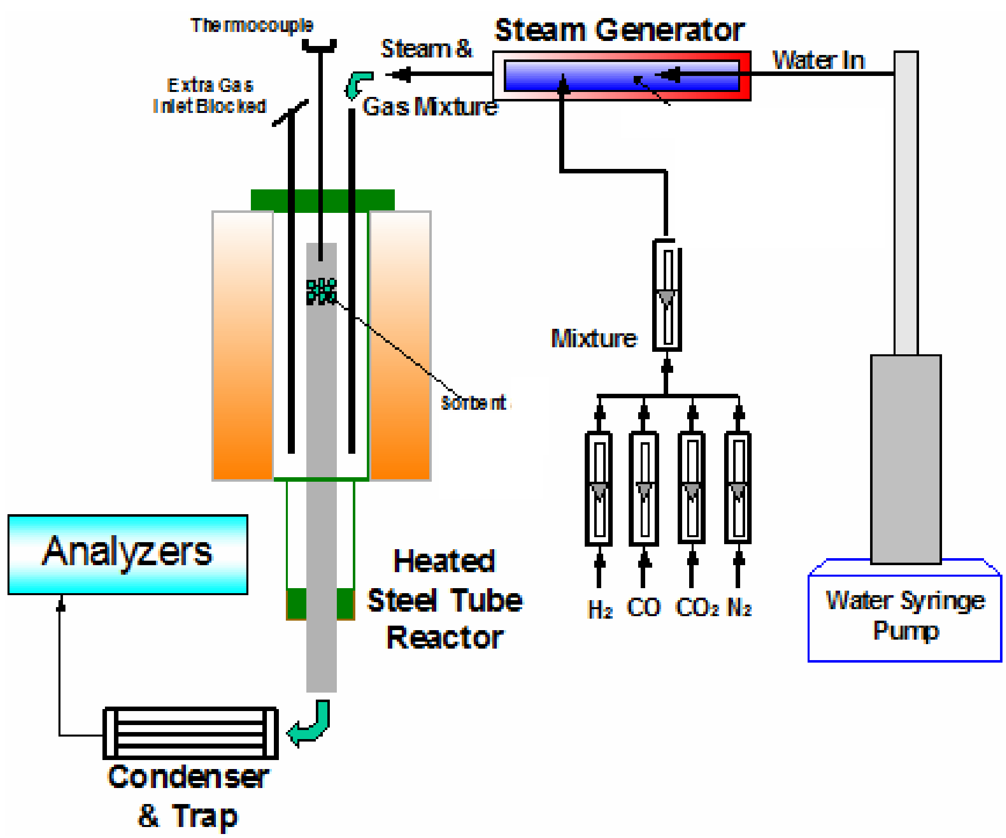

Figure 3.3. Laboratory Scale Fixed bed H_2 reactor

3.2 Safety

Safety is the number one issue when working in the laboratory. Personal Protective Equipment (PPE) such as safety goggles, lab coat, and closed-toed shoes were to be worn in the lab at all time. Generally this set of experimentation was relatively safe. However, there are a few extra safety precautions that should be pointed out. When working with the glacial, and even dilute, acetic acid, proper gloves were worn. When performing work with the TGA and fixed bed reactor, at times there were temperatures >600°C, therefore if the temperature was elevated, thermal gloves were worn. Also, the compressed gas cylinders were chained to the wall. And when in the lab while using CO, a CO detector was turned on to make sure there were no leaks. Lastly, the H_2 experiments require glasswool to be placed into the reactor tube, therefore loading of the reactor took place under a fume hood.

Chapter 4: Results and Discussion

To understand the results on CO_2 capture and H_2 production, the structure of the eggshell must be examined. Scanning Electron Microscope Images were compared for an untreated and a treated eggshell before any CCR cycle, after the first calcination, and then after the subsequent carbonation. As can be seen from Figure 4.1 (Iyer, 2006), the porosity of the acetic acid treated eggshell is much greater for each point of the cycle at 8000X magnification.

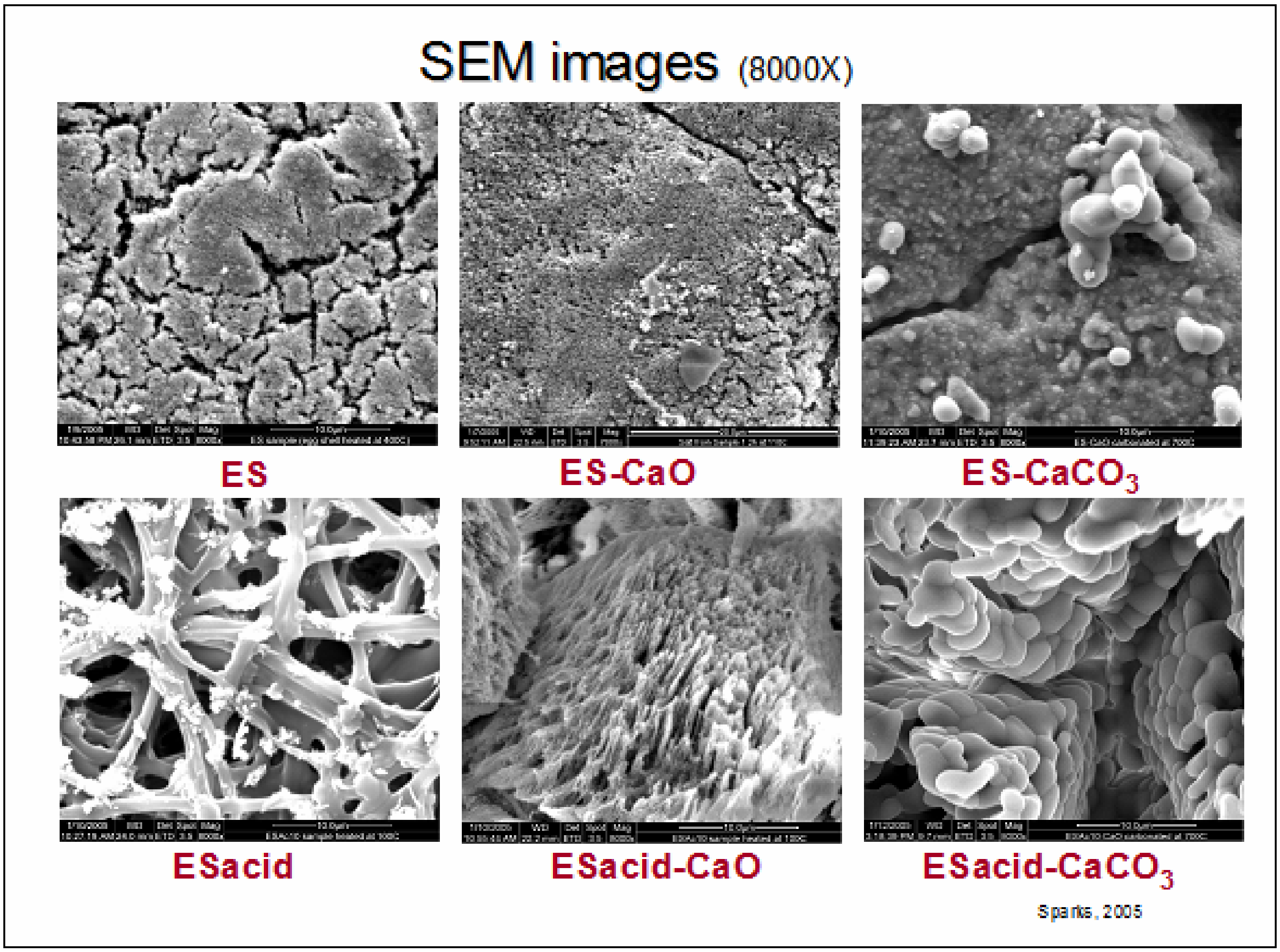

Figure 4.1 Scanning Electron Microscope Images of Untreated Eggshell and Acetic Acid Treated Eggshell for Each Stage of the First CCR cycle

4.1 CO_2 Capture Capacity

As explained in Experimental Procedure, a small 'chip' of eggshell is used in the TGA to determine CO_2 Capture Capacity of the eggshell sorbent in the presence of simulated flue gas. The reactivity can be determined over multiple cycles by measuring the weight of the sorbent. $CaCO_3$ and CaO have a molecular weight of 100 g/mol and 56 g/mol, respectively, thus causing the weight to increase during the carbonation reaction and decrease during the calcination phase; this can be seen in Figure 4.2. This particular experiment used roughly a 23 mg piece of shell in the presence of 10% CO_2 for 60 minute cycles at 700C. In the first cycle, the weight falls (calcination) and then when subjected to CO_2, the weight begins to rise again while it captures CO_2.

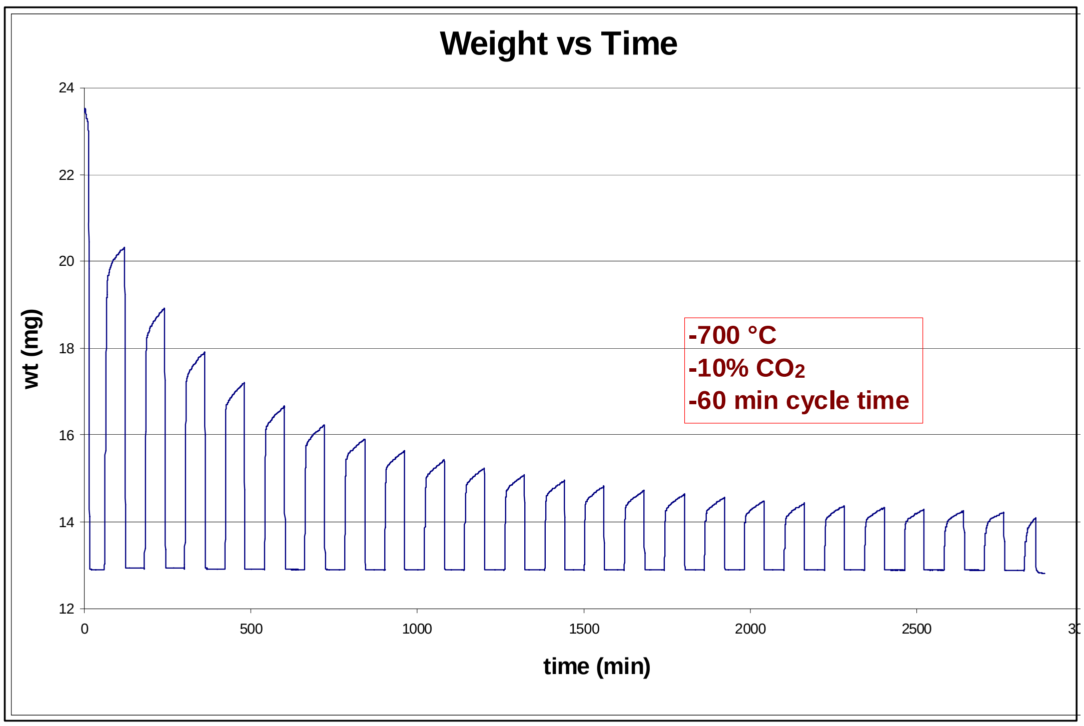

Figure 4.2. Carbon Dioxide Capture Capacity Using Eggshell: Weight vs Time

To be able to efficiently compare a particular sorbent to another one, it is better to compare the weight percent maximum of each cycle. However, the data is imported into an Excel file containing thousands of points, making it difficult and tedious to extract the maximum point from each cycle. Therefore, it was decided that it would be best to determine a more appropriate method using Matlab. The code written for the Excel file that contains multiple cycle capture capacity data to extract maximums and minimums of weight percent: (T. Vonder Haar)

```
function cap_time_data =
GetCycleCapture(filename,firstmax_time,cycle_time,sample_time)

%

search_radius = 5;

cycle = 1;

data = load(filename);

i = round(firstmax_time/sample_time)+1;
cap_time_data(cycle,1) = firstmax_time;
cap_time_data(cycle,2) = data(i,2);
i = i + round(2*cycle_time/sample_time);

while(i<length(data))
    cycle = cycle+1;
    data_window = data(i - search_radius:i + search_radius,:);
    [max_val,i_window] = max(data_window(:,2));
    i = round(data_window(i_window,1)/sample_time)+1;
    cap_time_data(cycle,1) = (i - 1)*sample_time;
    cap_time_data(cycle,2) = max_val;
    i = i + round(2*cycle_time/sample_time);

end
```

This allowed for a data extraction to generate graphs as shown in Figure 4.3.

Eggshells pre-treated with varying concentrations (1-10M) acetic acid and residence times (5-60 minute) were tested for reactivity over multiple cycles. Figure 4.3 shows the weight percent capture over multiple cycles for some of these varying treatments as well as an untreated sample.

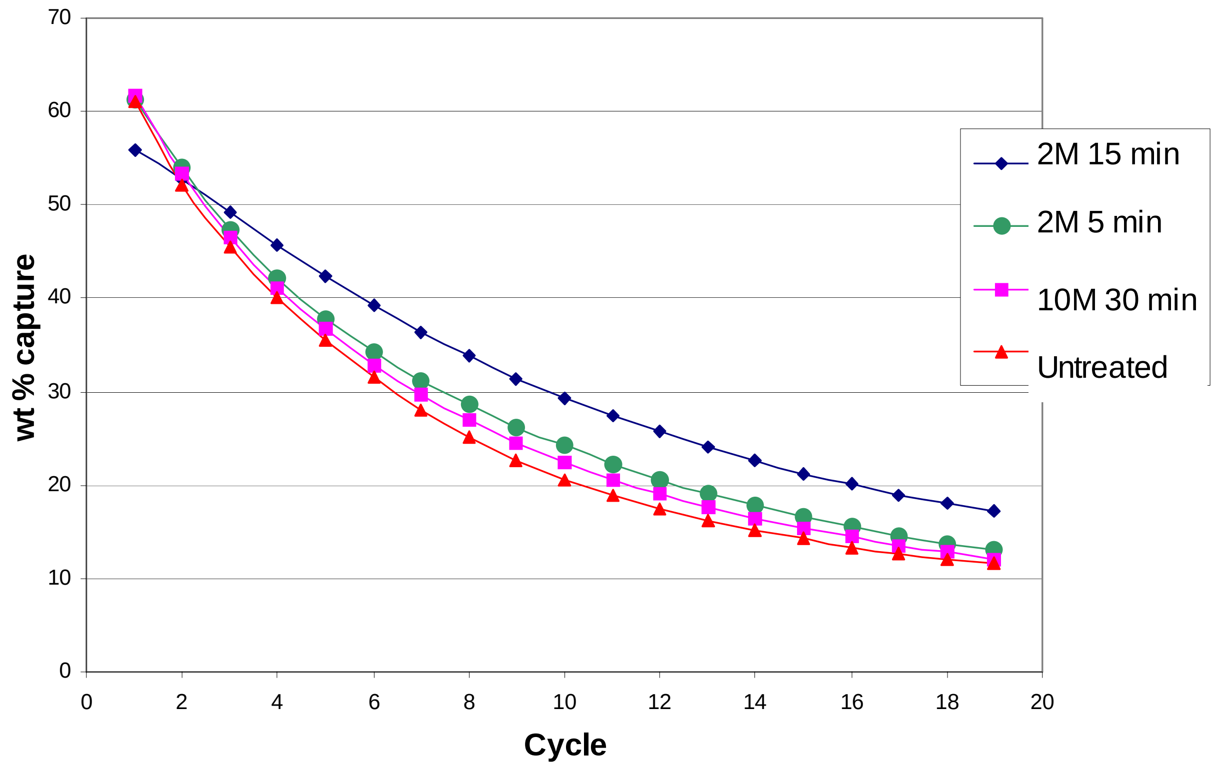

Figure 4.3. Weight Percent CO_2 Capture for Multiple Cycles: Varying Acetic Acid Concentrations and Residence Times

As can be seen from this figure, each of the treated eggshell samples performs better over multiple cycles than the untreated. The 2 molar- 15 minute sample has the best reactivity over time. This illustrates that there is an optimal treatment; subjecting the eggshell to the highest concentration or for the longest time period is not the best, and in fact, decreases the reactivity, however, it is necessary to have a significant period of time for reaction in an acetic acid solution. While attempting to optimize this treatment, it is also important to consider how well the pre-treatment facilitates the removal of the membrane. And while the longer time allowed for reaction or more concentrated solution does increase the separation of the membrane, it also begins to more noticeably affect the eggshell. The eggshell becomes very brittle and the pieces become hard to work with and break into even smaller pieces very easily. It was shown that 15-30 minutes in a 2 M solution does lead to enhanced removal.

Due to the reasons stated, concentrations of 1 and 2 M were further studied. Figure 4.4 displays data similar to Figure 4.3, but focuses on these concentrations. And again, it can be seen that the 2 M 15 minute sample performs the best.

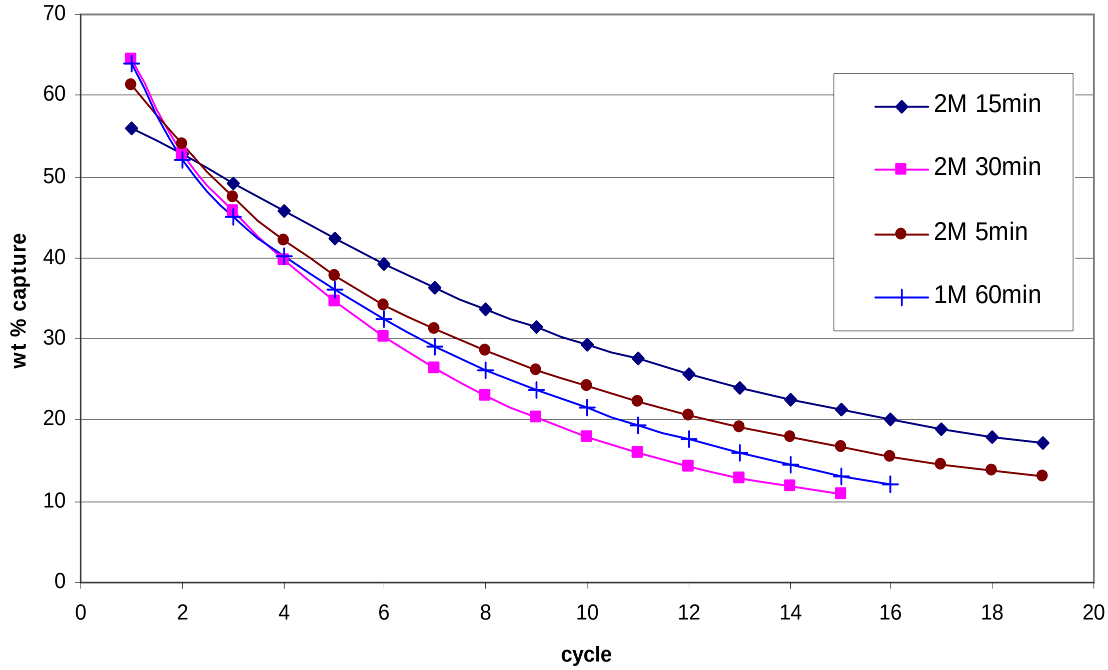

Figure 4.4. Weight Percent CO_2 Capture for Multiple Cycles: Varying Acetic Acid Concentrations (1 and 2 Molar) and Residence Times

It is important to understand that when utilized in a process such as a coal combustion facility, this sorbent will be recycled, thus imperative that the sorbent has a good capture capacity over multiple cycles. However, as seen from the data, the sorbent cannot be continuously regenerated, so fresh sorbent would be added during this process as well. Another aspect of this data that can be analyzed is the capture capacity for the first cycle. However, long-term reactivity is more important in this CO_2 separation scheme. Figure 4.5 shows the first cycle weight percent capture for an untreated sample and a 2M 15 and 30 minute. Although the 2 M 15 minute sample has shown to have increased capture capacity over multiple cycles, it does have a lower first cycle weight percent capture. To understand this, more SEM images are required because the structure of the sorbent is so important in the reactivity.

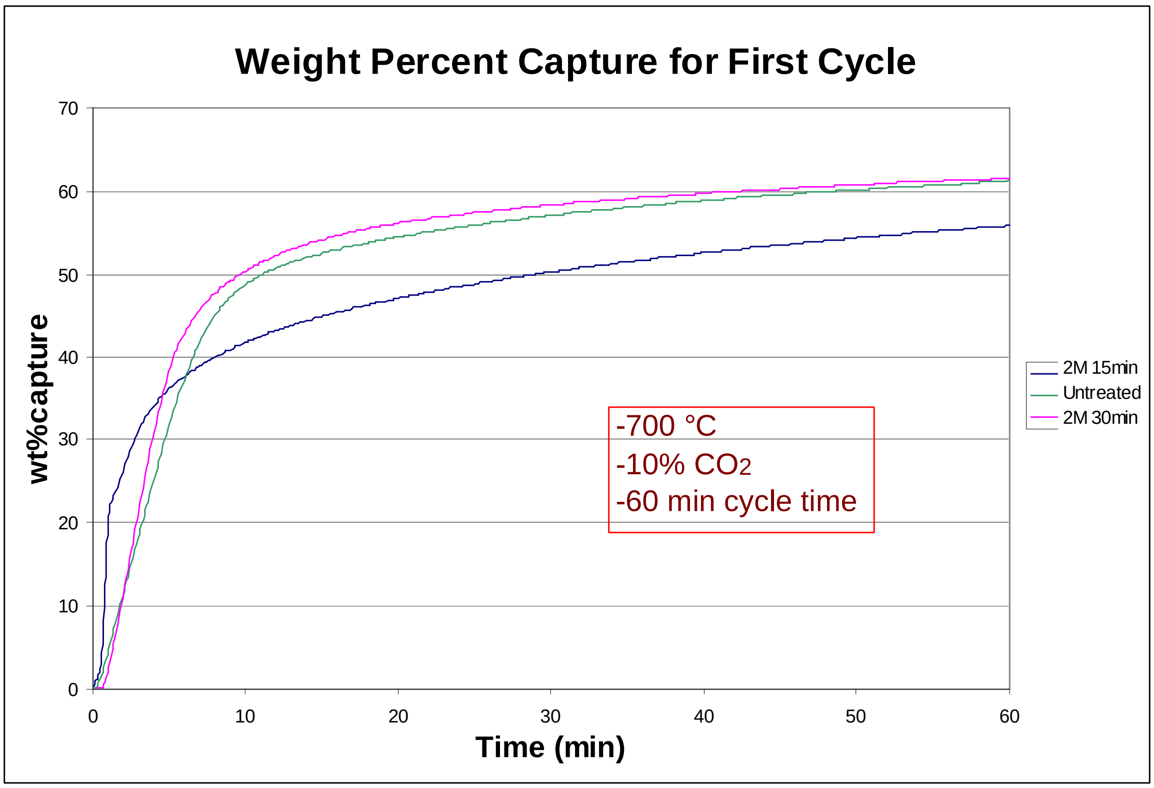

Figure 4.5. First Cycle Carbon Dioxide Capture Capacity Using Eggshell Sorbent

Other research that has been and is currently being conducted at OSU is testing different sorbents for CO_2 capture. Figure 4.6 (Iyer, 2006) is a comparison of some of these sorbents, along with traditional limestone, and three eggshell samples (untreated, hydrated and acetic acid treated). Details of the hydration procedure can be found in Angela Sparks' undergraduate thesis in 2005. This figure demonstrates that the treated eggshells perform better than limestone, and as explained earlier, do not have the same solid separation issues.

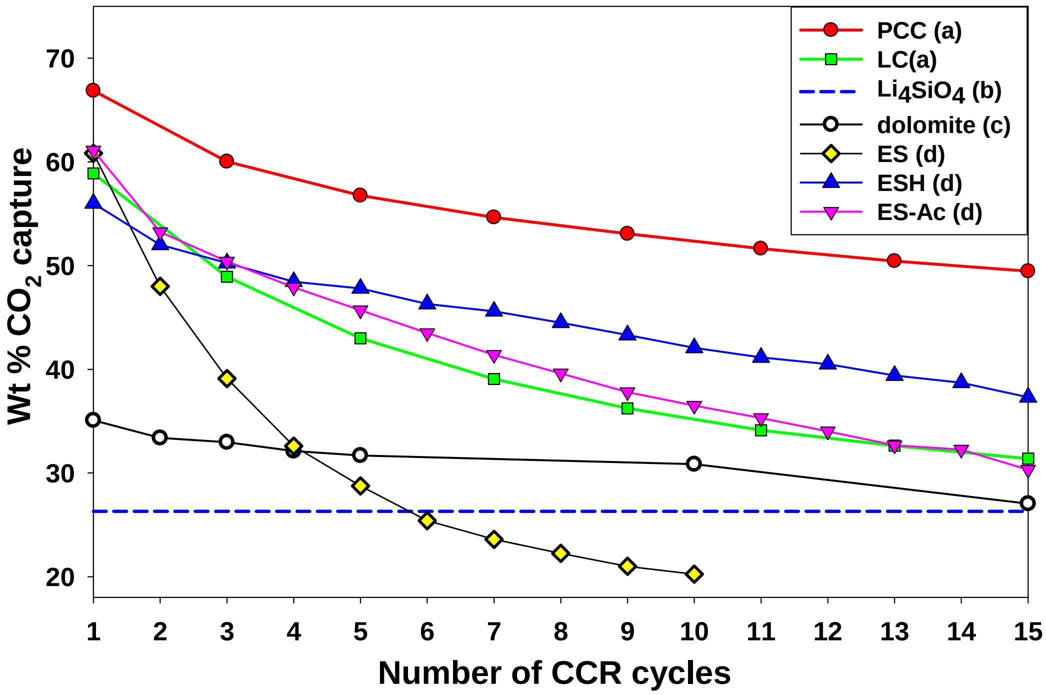

Figure 4.6. CO_2 Capture Capacity over Multiple Cycles for Various Sorbents

4.2 H_2 Production

As explained in Experimental Procedure, the gas stream leaving the fixed bed reactor for producing H_2 is analyzed. Figure 4.7 is an experiment using eggshell as a sorbent. As can be seen from the graph, near 100% conversion can be acheived, while after the sorbent is used up, the equilibrium composition is less than 40%. This shows the potential of utilizing eggshells as a sorbent in a coal gasification process for enhanced hydrogen production. It also implies that a catalyst, which is expensive and easily poisoned, does not have to be used.

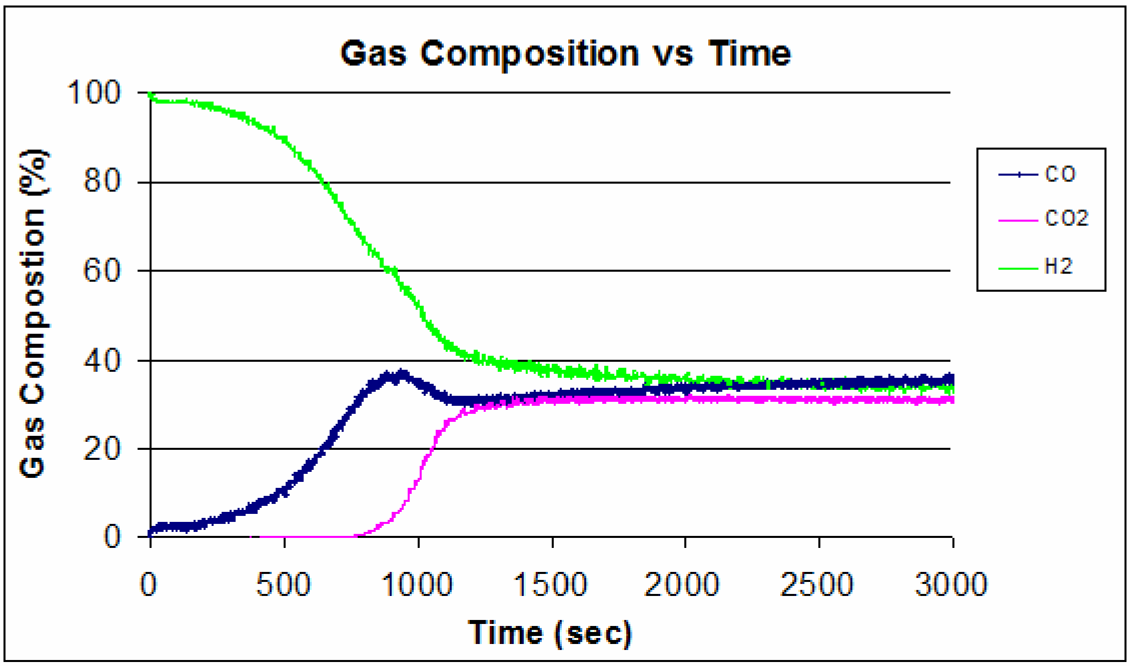

Figure 4.7 Gas Composition vs Time for H2 Production Utilizing Eggshell as a Sorbent

As previously stated, having an excess reactant can also drive the reaction toward H_2 production. This is demonstrated in Figure 4.8.

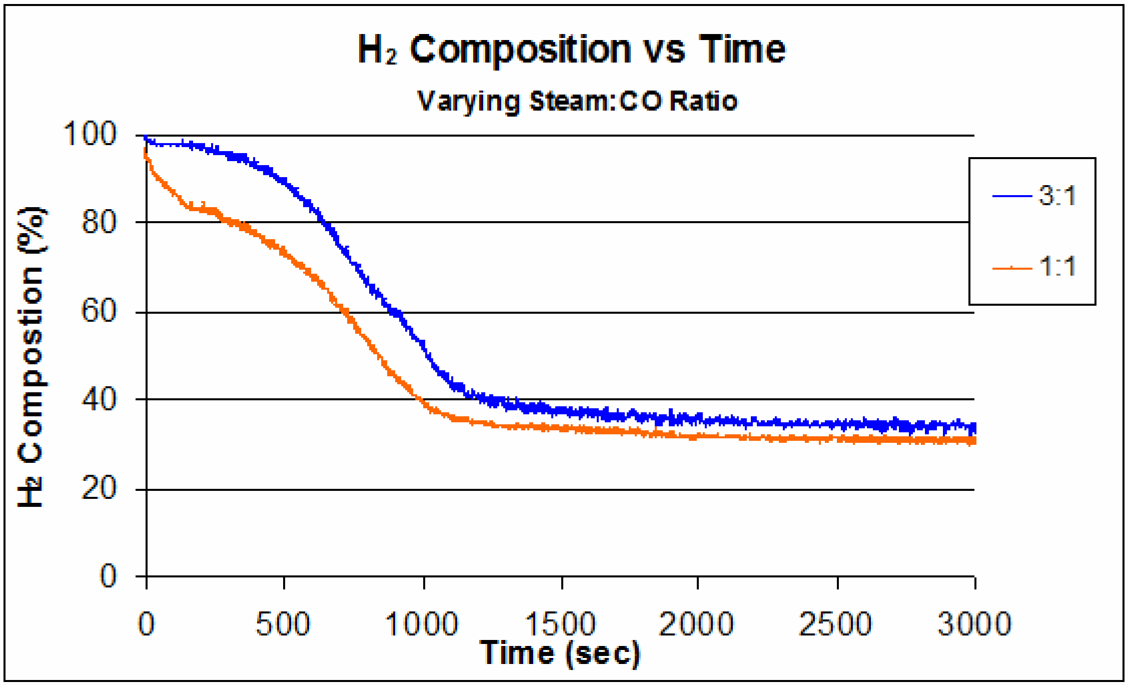

Figure 4.8 Gas Composition vs Time for H2 Production Utilizing Untreated Eggshell as a Sorbent: Varying Steam:CO Ratio

After verifying that the excess reactant did result in higher conversion, the next step was to verify if treating the eggshell had similar results to CO_2 capture, where in the results were better. The 2 M 15 min sample was chosen since it had the best results. Figure 4.9 does prove that acetic acid treated eggshell shows higher conversion.

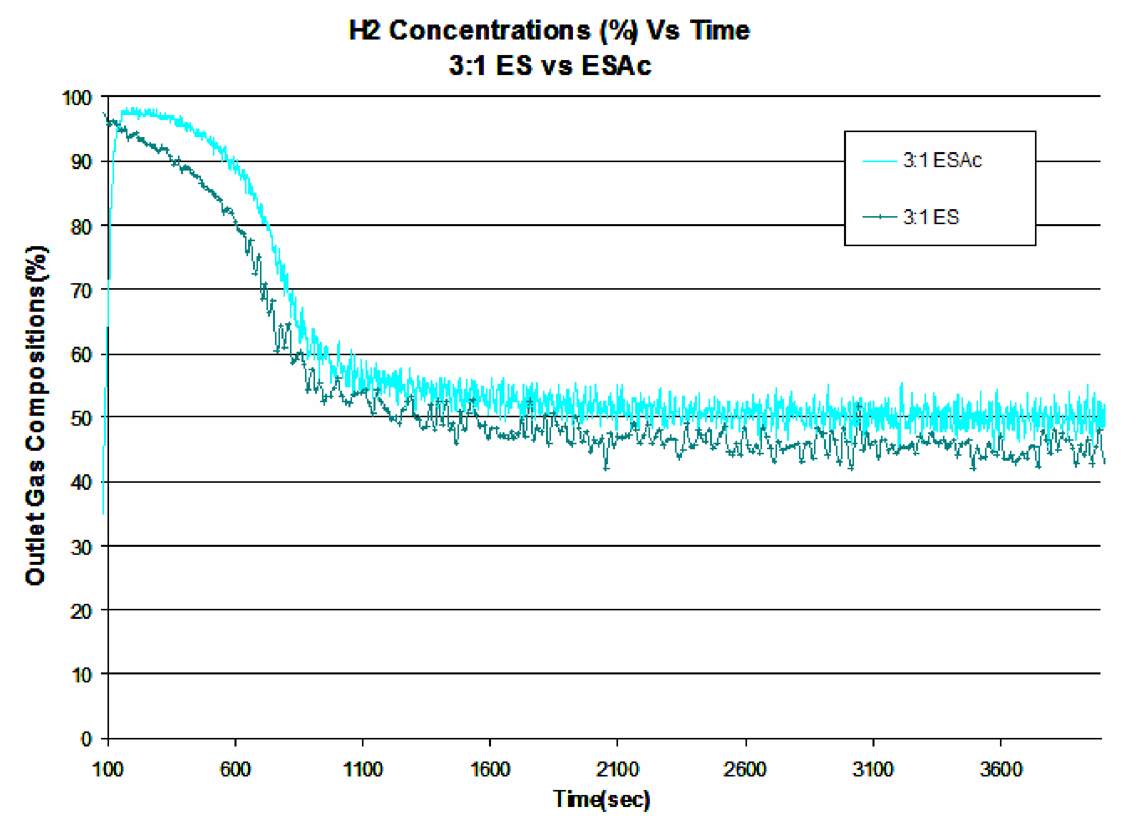

Figure 4.9 Gas Composition vs Time for H2 Production Comparing Untreated to Acetic Acid Treated Eggshell in 3:1 Steam to CO Ratios

Figure 4.10 represents both a 1:1 and 3:1 steam to CO ratio for acetic acid treated eggshell, and here, again, the experiment with the excess reactant has a higher outlet concentration of H_2.

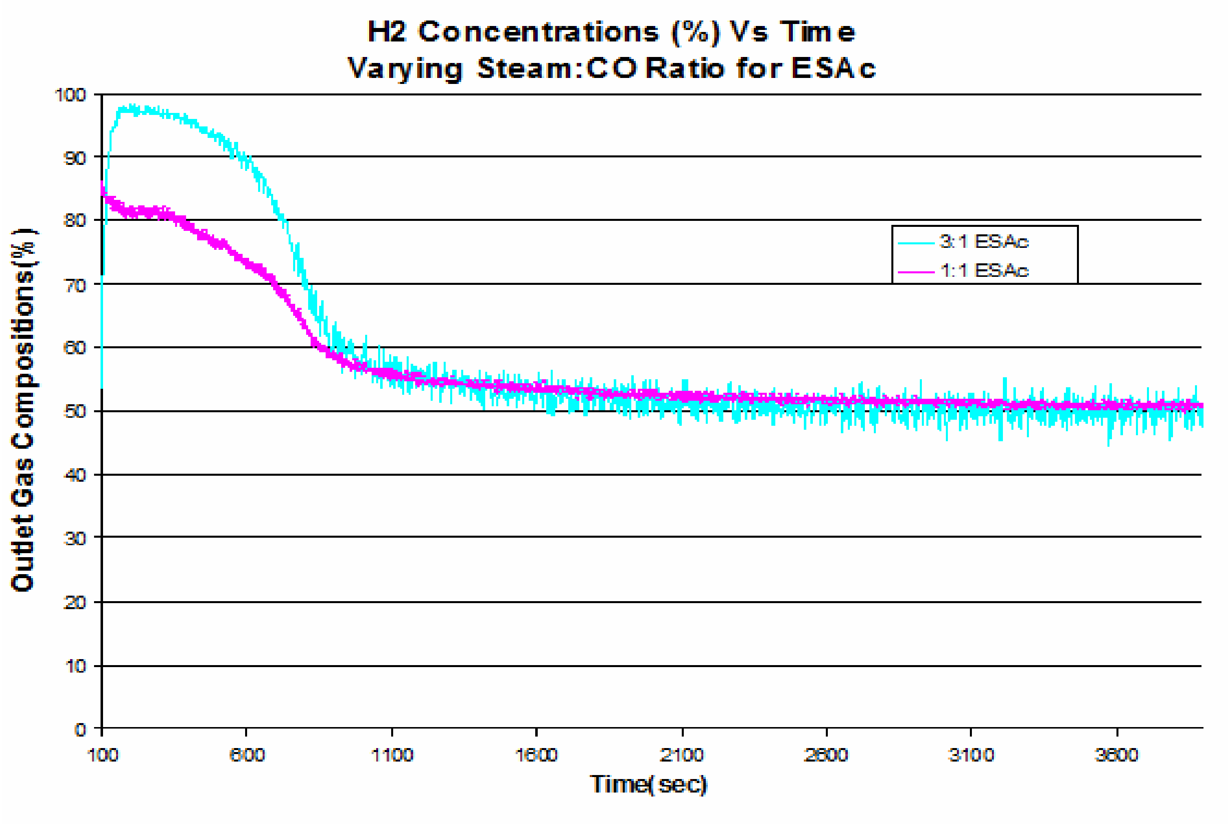

Figure 4.10 Gas Composition vs Time for H_2 Production Using Acetic Acid Treated Eggshell Comparing 3:1 and 1:1 Steam to CO Ratios

Chapter 5: Conclusions and Recommendations

5.1 Conclusions

There are some conclusions that can be drawn about the data obtained in these experiments. Eggshells are a natural agglomerate and can be utilized as a sorbent for carbon capture that is preferred over micron sized limestone sorbents that are able to mix with fly ash and prohibit reuse of the sorbent.

Treating with acetic acid increases porosity, and thus surface area, and leads to not only enhanced separation of the membrane from the eggshell but also increased reactivity over multiple cycles. For capture capacity over time, pre-treatment such as acetic acid and hydration has shown increase in reactivity. Further, a 15 minute residence time in 2 M acetic acid treated has shown the best performance through multiple cycles.

It is possible to achieve near 100% conversion of CO to H_2 product using eggshell as sorbent. The eggshell pre-treated with acetic acid shows a higher percent conversion, as does an increase in the steam to carbon monoxide ratio.

Collagen is contained within the eggshell membrane and can with relative ease be extracted. It used in various medical and cosmetics procedures and is extremely valuable if utilized to potential.

5.2 Recommendations

Products of coal combustion and coal gasification are not simply CO_2, and CO and H_2, respectively. Combustion produces such products as SO_2 and gasification H_2S, therefore it is recommended to investigate the parasitic effects of SO_2 and H_2S on CCR:

$$\mathbf{CaO + SO_2 + \frac{1}{2}\, O_2 \rightarrow CaSO_4} \qquad \textbf{(5)}$$

$$\mathbf{CaO + H_2S \rightarrow CaS + H_2O} \qquad \textbf{(6)}$$

As mentioned, there are other ways to drive the WGSR forward, such as subjecting the system to elevated pressures; therefore a suggestion is to perform H_2 production experiments under pressure. Also, it is recommended to perform testing on hydrated eggshells for H_2 production such as done in previous research for multiple cycle CO_2 capture. To optimize pre-treatment of acetic acid concentrations and residence time for H_2 production and then compare to CO_2 capture performance results is a recommendation. Other research has been conducted for various calcium-based materials for carbon capture, therefore it is recommended to examine further other calcium-based sorbents (oyster shells, etc) for H_2 production.

Determine exact amount of collagen in membrane and effects of acid on membrane (Mass Spectrometry Facility, Fontana Labs, OSU) and characterize acid solution after membrane removal for any released collagen. Another thing that would be useful is to obtain more SEM images for multiple samples throughout the mulitcyclic process to characterize the eggshell structure and porosity. The surface area, pore size and volume of the modified eggshells should be measured using the Brunaeur-Emmett-Teller (BET) analysis.

Lastly, it would be extremely beneficial to determine a way to integrate this project with an egg processing company and the utility industry. One thing to consider when doing this is the scale-up of the acetic acid treatment, particularly the rinsing of the shells and membranes after treatment and finding a way of separating the CO_2 bubbles from the acetic acid solution.

Overall, this project has shown encouraging results for carbon dioxide capture along with enhanced hydrogen production utilizing an economical sorbent, both which have great local, national, and global impacts. Also, these recommendations, when completed, would be beneficial for further understanding of this project as well as being closer to being able to employ this project on a larger scale.

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